

Article principal
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la T H E S E présentée
pour l'obtention
du grade de DOCTEUR ES SCIENCES PHYSIQUES
à L'UNIVERSITE PIERRE ET MARIE CURIE
- PARIS 6 -

par Osman ATABEK

Sujet de la Thèse : Interactions multicontinuum dans quelques
problèmes de collisions moléculaires.

Soutenue le 12 Mai 1976
Devant le Jury composé de :

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Reaction operators for the relative coordinates treatment of atom-diatom collinear collisions

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The reaction operator $\mathbf{K}$ is used to treat the collinear collision between an atom and a diatom in relative coordinates representation. With this choice of coordinates the coupling between the zeroth-order channels is due to a kinetic crossing term. The inadequacy of the channel functions to describe properly the asymptotic motion can be partially corrected by a renormalization procedure consisting of a shift of the energies. An analytical solution for arbitrary inter-continuum couplings can be given for the $\mathbf{T}$ matrix when the diatom is approximated by a harmonic oscillator. Calculations are presented for two types of atom-diatom interaction potential: an exponential or a Morse function. The results are compared with the exact available numerical calculations and with the linearized distorted wave approximation. The treatment in relative coordinates with renormalization is found to yield, for many cases of physical significance, very good results.

1. INTRODUCTION

Recent theoretical studies of photodissociation and predissociation of triatomic molecules [1, 2] have considered an initial discrete state relaxing into a manifold of coupled continua. An explicit expression for the vibrational distribution of fragments was obtained when the intercontinuum perturbation only couples adjacent continua. This occurs in the relative coordinates treatment of a linear triatomic system ABC, in the harmonic approximation, when the Rosen [3] partition of the hamiltonian is used.

The same multicontinuum problem appears in the energy transfer between vibrational and translational degrees of freedom in atom-diatom collisions. In this latter case the system is initially in a continuum describing the asymptotic motion when the atom is far away from the oscillator, and the problem is to find the vibrational distribution of the diatomic after the collision. This problem has been solved numerically [4, 5] for the collinear collision of a particle A and

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a harmonic oscillator BC, neglecting the interaction between particles A and C and taking for the potential V_{AB} a repulsive exponential curve [4] or a Morse potential [5]. Several approximate methods have also been used to handle this problem: (a) First-Order Distorted Wave Approximation (FODWA) [6, 7], (b) $\mathbf{K}$ matrix in Distorted Wave Approximation (KDWA) [8], (c) Adiabatic approximation [9].

Recently [10] some comparisons have been made between the exact or the approximate results listed above and the first-order Born approximation using the Rosen partition of the hamiltonian in the relative coordinates representation. The perturbation is a kinetic crossing term in the R_{AB} and R_{AC} coordinates, which does not vanish at infinity. Consequently the asymptotic states are not well-behaved and it is necessary to work out a renormalization procedure in order to describe properly the asymptotic motion. This renormalization can be achieved approximately just by shifting the energies of the states and this is equivalent to evaluating the probabilities with matrix elements of the perturbation between non-resonant states. The results for a wide range of parameters are in good agreement with the exact calculations for sufficiently low energies. At high energies the first-order probabilities diverge and become even larger than unity, but this state of affairs is common to all first-order treatments in the Born approximation. This divergence can be avoided by using the $\mathbf{K}$ matrix formalism [8 (a), 11, 12 (a), (b)], which is one of the exponentiation schemes ensuring automatically the unitarity of the $\mathbf{S}$ matrix [12 (b)]. The first-order approximation for the $\mathbf{K}$ matrix is equivalent to taking all the couplings independent of energy with unbounded continua, that is to neglect all the principal part distributions appearing in the Born expansion. The leading terms in this expansion can be summed up and an $\mathbf{S}$ matrix is obtained which is unitary.

In the present paper we present $\mathbf{K}$ matrix calculations for the Rosen partition of the hamiltonian for the collinear collision of a particle with a harmonic oscillator utilizing different forms for the atom-diatom interaction potential. Explicit formulae were obtained for the probability of translational-vibrational energy transfer and compared with the results of exact results and with other approximate methods.

2. THE UNPERTURBED HAMILTONIAN

The Schrödinger equation describing the collision between a particle A and a harmonic oscillator BC is, in terms of dimensionless quantities [4],

$$\left\{ -\frac{1}{2m} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2 + U(x-y) \right\} |\psi_E(x, y)\rangle = E |\psi_E(x, y)\rangle \quad (2.1)$$

with $m = m_A m_C / (m_A + m_B + m_C)$; in this hamiltonian the motion of the centre of mass of the whole system has already been separated and x is a dimensionless coordinate proportional to the distance between particle A and the centre of mass of the oscillator BC, while y corresponds to the distance between particles B and C. The energy E and the potential U are measured in units of $\hbar\omega_{BC}$.

Let us now write the hamiltonian in the relative coordinates between particles: $R_{AB} = R_A - R_B$ and $R_{BC} = R_B - R_C$. The dimensionless quantities associated

with these coordinates are $z=x-y$ and y . In this representation the wave equation takes the form

$$\left\{ -\frac{1}{2\bar{m}} \frac{\partial^2}{\partial z^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2 + U(z) + \frac{\partial^2}{\partial y \partial z} \right\} |\psi_E(y, z)\rangle = E |\psi_E(y, z)\rangle \quad (2.2)$$

with

$$\bar{m} = m/(m+1). \quad (2.3)$$

In the Rosen partition method [3] the unperturbed hamiltonian is taken to be

$$H_0 = -\frac{1}{2\bar{m}} \frac{\partial^2}{\partial z^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2 + U(z) \quad (2.4)$$

and the perturbation is the kinetic crossing term

$$V = H - H_0 = \frac{\partial^2}{\partial y \partial z}. \quad (2.5)$$

H_0 is now separable in the coordinates y and z . Its eigenfunctions can be written :

$$|\psi_{nE}^0(y, z)\rangle = |\chi_n(y)\rangle |\phi_{nE}(z)\rangle, \quad (2.6)$$

$|\chi_n(y)\rangle$ being the harmonic oscillator wavefunction of energy $(n + \frac{1}{2})$ and $|\phi_{nE}(z)\rangle$ the solution of

$$\left\{ -\frac{1}{2\bar{m}} \frac{\partial^2}{\partial z^2} + U(z) - (E - n - \frac{1}{2}) \right\} |\phi_{nE}(z)\rangle = 0. \quad (2.7)$$

The potential $U(z)$ goes to zero as $z \rightarrow \infty$. Thus, asymptotically

$$|\psi_{nE}^0(y, z)\rangle \underset{z \rightarrow \infty}{\simeq} |\chi_n(y)\rangle C_{nE} \cos(\bar{k}_{nE} z + \bar{\varphi}_{nE}), \quad (2.8)$$

where

$$\bar{k}_{nE} = [2\bar{m}(E - n - \frac{1}{2})]^{1/2}. \quad (2.9)$$

Now we know that the true eigenfunctions of the total hamiltonian (2.1) have the asymptotic behaviour

$$|\psi_{nE}(y, x)\rangle \underset{x \rightarrow \infty}{\simeq} |\chi_n(y)\rangle A_{nE} \cos(k_{nE} x + \varphi_{nE}), \quad (2.10)$$

where k_{nE} has the same expression as in (2.9) but with m replacing $\bar{m}$. For $m \ll 1$, $\bar{m} \sim m$, the two asymptotic expressions (2.8) and (2.10) have approximately the same energy, but for a general m there is an energy shift

$$\delta_n(E) = m(E - n - \frac{1}{2}) \quad (2.11)$$

between the zero-order wavefunctions $|\psi_{nE}^0\rangle$ defined above, and the true eigenfunctions $|\psi_{nE}\rangle$ of the total hamiltonian. This shift is due to the fact that the perturbation $\partial^2/\partial y \partial z$ does not vanish at infinity and leads to persistent effects such as those encountered in quantum field theories [13, 14]. In Appendix A we show that the inter-continuum coupling behaves as a principal part

distribution, irrespective of the particular potential chosen for the AB interaction. In reference [10] it was argued that such couplings lead to the appearance of singular terms in the expression of the resolvent operator. These have to be summed-up, leading ultimately to a renormalization of the energy and a redefinition of the asymptotic states. This is a very difficult mathematical problem in our case. A simplified procedure consists [10] in merely shifting the zero-order eigenfunctions (2.8) by the quantity defined by (2.11), and proceeding to the usual perturbation methods with these shifted eigenfunctions. The effect of this shift is to transform $\bar{k}_{nE}$ into $k_{nE'}$, i.e. to put m in place of $\bar{m}$ in (2.9). The shift means that in order to describe a collision with a given initial relative kinetic energy for the pair A, BC one must use a different kinetic energy for the pair A, B. Such considerations are also present in the semi-classical ITFITS method [15], for the same reason, that is the use of relative coordinates.

It was already shown [10] that this renormalization procedure gives good results in the first-order Born approximation, for the case of a repulsive exponential interaction [10 (a)] and for a Morse potential [10 (b)] when the energy is sufficiently low. For higher energies, probabilities are much overestimated and can exceed unity. This is due, of course, to the use of the first-order Born approximation which does not ensure the unitarity of the **S** matrix.

From the formal theory of scattering [11] we know that the exact probabilities are given by

$$P_{nn'}(E) = |S_{nn'}(E)|^2 \equiv |\delta_{nn'} - 2i\pi T_{nn'}(E)|^2, \quad (2.12)$$

where $T_{nn'}(E)$ is the matrix element between unperturbed eigenfunctions corresponding to channels n and n' at energy E of the so-called transition operator :

$$\mathbf{T} = V + \lim_{\epsilon \rightarrow 0^+} V[E - H_0 + i\epsilon]^{-1} \mathbf{T}. \quad (2.13)$$

$P_{nn'}(E)$ denotes the probability of finding the system in the channel n at time $t = +\infty$, if at $t = -\infty$ the system was in channel n' , with energy E , and the colliding particles were far away from the interaction region. Equation (2.13) can be solved by iteration :

$$\mathbf{T} = V + VG_0^+V + VG_0^+VG_0^+V + \dots \quad (2.14)$$

with $G_0^+ = [E - H_0 + i\epsilon]^{-1}$ and $\epsilon \rightarrow 0^+$. Retaining the first term gives the first-order Born approximation :

$$P_{nn'} = |\delta_{nn'} - 2i\pi V_{nE, n'E}|^2 \quad (2.15)$$

which has been used in reference [10]. Now writing formally

$$\mathbf{T} = \mathbf{K} - i\pi \mathbf{K} \delta(E - H_0) \mathbf{T} \quad (2.16)$$

it follows from (2.14), that

$$\begin{aligned} \mathbf{K} &= V + V\mathcal{P} \left(\frac{1}{E - H_0} \right) \mathbf{K}, \\ \mathbf{K} &= V + V\mathcal{P} \left(\frac{1}{E - H_0} \right) V + V\mathcal{P} \left(\frac{1}{E - H_0} \right) V\mathcal{P} \left(\frac{1}{E - H_0} \right) V + \dots \end{aligned} \quad (2.17)$$

This operator is the so-called 'reaction operator' and the equation (2.16) is often referred to as the 'Heitler relation' [12]. At first sight (2.16) provides only an alternative way of writing the same transition operator $\mathbf{T}$. However, the importance of the reaction operator $\mathbf{K}$ is that any truncation in the development (2.17) always produces an $\mathbf{S}$ matrix which is unitary. This is an important condition in order to have probability conservation. To show this let us define [12] the $N \times N$ matrices (N being the number of open channels) :

$$\mathcal{T} \equiv \{T_{nn'}(E)\}; \quad \mathcal{K} \equiv \{K_{nn'}(E)\}; \quad \mathcal{S} \equiv \{S_{nn'}(E)\}; \quad \mathbf{1} \equiv \{\delta_{nn'}\} \quad (2.18)$$

Now, from (2.12) and (2.16) :

$$\mathcal{S} = \mathbf{1} - 2i\pi\mathcal{T}; \quad \mathcal{T} = \mathcal{K} - i\pi\mathcal{K}\mathcal{T}, \quad (2.19)$$

thus

$$\mathcal{T} = [\mathbf{1} - i\pi\mathcal{K}]^{-1}\mathcal{K} \quad (2.20)$$

and

$$\mathcal{S} = [\mathbf{1} - i\pi\mathcal{K}]^{-1}[\mathbf{1} + i\pi\mathcal{K}]^{-1}. \quad (2.21)$$

Now, it is very easy to show, using (2.21), that $\mathcal{S}$ is unitary for any hermitian matrix $\mathcal{K}$, and in particular if we take the first approximation of (2.17) :

$$\mathbf{K} = V. \quad (2.22)$$

In this case the Heitler equation (2.16) becomes :

$$\mathbf{T} = V - i\pi V\delta(E - H_0)\mathbf{T} \quad (2.23)$$

An explicit solution of this equation can be given for V coupling only adjacent continua. This is done in § 5, and Appendix B.

3. COMPARISON BETWEEN THE ROSEN PARTITION AND AN ADIABATIC APPROACH

We would like to point out that an approach based on the Rosen partition is closely related to a treatment of the collision which starts from an adiabatic formulation, where the 'slow' motion is that of the oscillator and the 'fast' motion that of the incident atom. Thus this adiabatic description is the reverse of that considered by Thiele and Katz [9], where one has to consider first of all the motion of the oscillator for a fixed position of the external atom. Our comparison will be based on the derivation for both approaches of secular equations describing configuration interaction.

3.1. The Rosen equations

We write the solution of the wave equation in the form

$$|\psi_E(y, z)\rangle = \sum_{n'} \int dE' A_{n'E'}(E) |\psi_{n'E'}^0(y, z)\rangle \quad (3.1)$$

with $|\psi_{nE}^0(y, z)\rangle$ defined by (2.6). Introduction of (3.1) into the wave equation results in the secular equations

$$\begin{aligned} & [E' - E]A_{n'E'}(E) \\ &= - \sum_{n'} \int dE'' A_{n''E''}(E) \left\langle \chi_{n'} \left| \frac{\partial \chi_{n''}}{\partial y} \right\rangle_y \left\langle \phi_{n'E'} \left| \frac{\partial \phi_{n''E''}}{\partial z} \right\rangle_z \right. \end{aligned} \quad (3.2)$$

3.2. Adiabatic description

The hamiltonian is written in the x and y coordinates (cf. (2.11)). Neglecting the kinetic energy of the oscillator we solve the y -dependent wave equation for the external particle :

$$\left[-\frac{1}{2m} \frac{\partial^2}{\partial x^2} + U(x-y) + \frac{1}{2}y^2 \right] |\varphi_k(x, y)\rangle = W(y) |\varphi_k(x, y)\rangle \quad (3.3)$$

with

$$W(y) = \frac{k^2}{2m} + \frac{1}{2}y^2. \quad (3.4)$$

We assume that the solutions of (3.3) are k -normalized, i.e.

$$\langle \varphi_k(x, y) | \varphi_{k'}(x, y) \rangle_x = \delta(k - k'). \quad (3.5)$$

The solution of the complete wave equation is now written

$$|\psi_E(y, x)\rangle = \sum_{n'} \int dk' B_{n'k'}(E) |\chi_{n'}(y)\rangle |\varphi_{k'}(x, y)\rangle, \quad (3.6)$$

where $\chi_{n'}(y)$ is the free oscillator wave function ; this leads to the secular equations

$$\begin{aligned} \left[\frac{k'^2}{2m} + n' + \frac{1}{2} - E \right] B_{n'k'}(E) &= \sum_{n''} \int dk'' B_{n''k''}(E) \left\langle \chi_{n'} \left| \frac{\partial \chi_{n''}}{\partial y} \right\rangle_y \right. \\ &\times \left\langle \varphi_{k'}(x, y) \left| \frac{\partial \varphi_{k''}(x, y)}{\partial y} \right\rangle_x + \frac{1}{2} \int dk'' B_{n'k''}(E) \left\langle \varphi_{k'} \left| \frac{\partial^2 \varphi_{k''}}{\partial y^2} \right\rangle_x \right. \end{aligned} \quad (3.7)$$

Since U of equation (3.3) is a function of $(x-y)$, we have

$$|\varphi_k(x, y)\rangle \equiv |\varphi_k(x-y)\rangle$$

and therefore

$$\left\langle \varphi_{k'} \left| \frac{\partial^2 \varphi_{k''}}{\partial y^2} \right\rangle_x = \left\langle \varphi_{k'} \left| \frac{\partial^2 \varphi_{k''}}{\partial x^2} \right\rangle_x. \quad (3.8)$$

According to (3.3) we have

$$\left\langle \frac{\partial^2 \varphi_k}{\partial x^2} \right\rangle = -[k^2 - 2mU(x-y)] |\varphi_k\rangle \quad (3.9)$$

and thus

$$\left\langle \varphi_{k'} \left| \frac{\partial^2 \varphi_{k''}}{\partial y^2} \right\rangle_x = -k'^2 \delta(k' - k'') + 2m \langle \varphi_{k'} | U(x-y) | \varphi_{k''} \rangle_x. \quad (3.10)$$

This relation indicates that there is a diagonal correction which can be incorporated into the left-hand side. The secular equations have now the form

$$\begin{aligned} \left[\frac{k'^2}{2m} + \frac{k'^2}{2} + n' + \frac{1}{2} - E \right] B_{n'k'}(E) &= - \sum_{n''} \int dk'' B_{n''k''}(E) \left\langle \chi_{n'} \left| \frac{\partial \chi_{n''}}{\partial y} \right\rangle_y \right. \\ &\times \left\langle \varphi_{k'} \left| \frac{\partial \varphi_{k''}}{\partial x} \right\rangle_x + m \int dk'' B_{n'k''}(E) \langle \varphi_{k'} | U | \varphi_{k''} \rangle_x. \end{aligned} \quad (3.11)$$

We remark that the diagonal correction has changed the zeroth-order energy into $k'^2/2\bar{m} + n' + \frac{1}{2}$, which is the energy E' of the Rosen formulation. The first term of the right-hand side is in close correspondence with the right-hand side of (3.2), since

$$\left\langle \varphi_{k'} \left| \frac{\partial \varphi_{k''}}{\partial x} \right\rangle_x = \left\langle \varphi_{k'} \left| \frac{\partial \varphi_{k''}}{\partial z} \right\rangle_z.$$

The second term is equivalent to an intracontinuum coupling. In the limit of small m the two systems of secular equations will coincide, and since in this case $|\phi_{nE}\rangle$ and $|\varphi_k\rangle$ become identical, apart from a normalization factor, $A_{n'E'}(E)$ is proportional to $B_{n'k'}(E)$.

The analogy between the two treatments is not to be taken to mean that we consider the collision to be adiabatic with the oscillator having the slower motion, since the excitation probabilities are assigned to deviations from this adiabatic treatment.

4. THE CONTINUUM-CONTINUUM COUPLING AND THE RELATION WITH THE LINEARIZED VERSION OF FODWA

The inter-continuum coupling is

$$\begin{aligned} V_{nE, n'E'} &= \left\langle \psi_{nE}^0(y, z) \left| \frac{\partial^2}{\partial y \partial z} \right| \psi_{n'E'}^0(y, z) \right\rangle \\ &= \left\langle \chi_n(y) \left| \frac{\partial}{\partial y} \right| \chi_{n'}(y) \right\rangle_y \left\langle \phi_{nE}(z) \left| \frac{\partial}{\partial z} \right| \phi_{n'E'}(z) \right\rangle_z, \end{aligned} \quad (4.1)$$

where use has been made of the definitions (2.5) and (2.6). It is very easy to see now that this perturbation only couples adjacent continua. From the definition of creation and annihilation operators for a harmonic oscillator, we have

$$\frac{\partial}{\partial y} = 2^{-1/2}[a - a^\dagger] \quad (4.2)$$

thus

$$\left\langle \chi_n \left| \frac{\partial}{\partial y} \right| \chi_{n'} \right\rangle_y = (n'/2)^{1/2} \delta_{n, n'-1} - [(n'+1)/2]^{1/2} \delta_{n, n'+1}. \quad (4.3)$$

The last factor in (4.1) can be transformed using the general identity

$$\left\langle \phi_{nE} \left| \frac{\partial}{\partial z} \right| \phi_{n'E'} \right\rangle_z = (2\bar{m})(\bar{k}_{nE}^2 - \bar{k}_{n'E'}^2)^{-1} \left\langle \phi_{nE} \left| \left(\frac{\partial U}{\partial z} \right) \right| \phi_{n'E'} \right\rangle_z. \quad (4.4)$$

We have to specify now the potential $U(z)$ in order to calculate these matrix elements. But first we are going to show that a close relation exists between these matrix elements and the couplings calculated in the linearized version of the distorted-wave treatment. In the general distorted wave approach [16] the wavefunction $|\psi_E(x, y)\rangle$ defined by the Schrödinger equation (2.1) is expanded in terms of the unperturbed oscillator wave-functions $|\chi_n(y)\rangle$

$$|\psi_E^{\text{DW}}(x, y)\rangle = \sum_n |\phi_{nE}(x)\rangle |\chi_n(y)\rangle \quad (4.5)$$

which gives, after substitution in equation (2.1), the coupled equations

$$\left[-\frac{1}{2m} \frac{\partial^2}{\partial x^2} + U_{nn}(x) + \frac{k_{nE}^2}{2m} \right] |\phi_{nE}(x)\rangle = -\sum_{n' \neq n} U_{nn'}(x) |\phi_{n'E}(x)\rangle, \quad (4.6)$$

where $k_{nE}^2 = 2m(E - n - \frac{1}{2})$ and $U_{nn'}(x) = \langle \chi_n(y) | U(x-y) | \chi_{n'}(y) \rangle_y$. We can now write formally $H = H_0^{\text{DW}} + V^{\text{DW}}$, with

$$H_0^{\text{DW}} = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2 + V_0(x), \quad (4.7)$$

where $V_0(x)$ is the diagonal part of $U_{nn'}(x)$ and V^{DW} is the non-diagonal part. In the linearized version of this approximation $U(x-y)$ is expanded around the equilibrium position $y=0$, and only the linear term is retained :

$$U(x-y) = U(x) + \left. \frac{\partial U}{\partial y} \right|_{y=0} y. \quad (4.8)$$

The harmonic oscillator selection rules gives for the zero-order hamiltonian

$$H_0^{\text{DW}} = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2 + U(x) \quad (4.9)$$

and the perturbation is

$$V^{\text{DW}} = \left. \frac{\partial U}{\partial y} \right|_{y=0} y. \quad (4.10)$$

Now

$$y = 2^{-1/2} [a + a^\dagger] \quad (4.11)$$

and, due to the fact that U is only a function of the difference $(x-y)$, $\partial U / \partial y = -\partial U / \partial x$. Thus :

$$V^{\text{DW}}_{nE, n'E'} = \{(n'/2)^{1/2} \delta_{n, n'-1} + [(n'+1)/2]^{1/2} \delta_{n, n'+1}\} \times \left\langle \phi_{nE}^{\text{DW}} \left| \frac{\partial U}{\partial x} \right| \phi_{n'E'}^{\text{DW}} \right\rangle_x. \quad (4.12)$$

Comparing this expression with the matrix elements in the relative coordinates treatment, given by the product of expressions (4.3) and (4.4), we see that a close relation exists. This is very useful to calculate the couplings (4.1) by adapting the expressions calculated in the distorted-wave approximation for an exponential interaction [6 (a)] or a Morse potential [7 (a)]. This calculation gives [10]

(i) for a purely repulsive exponential potential of the form

$$U(z) = A \exp(-\alpha z) :$$

$$\begin{aligned} \left\langle \phi_{nE} \left| \frac{\partial}{\partial z} \right| \phi_{n'E'} \right\rangle_z &= \frac{2\bar{m}}{\alpha} \left[\sinh \left(\frac{2\pi}{\alpha} k_{nE} \right) \sinh \left(\frac{2\pi}{\alpha} k_{n'E'} \right) \right]^{1/2} \\ &\times \left[\cosh \left(\frac{2\pi}{\alpha} k_{nE} \right) - \cosh \left(\frac{2\pi}{\alpha} k_{n'E'} \right) \right]^{-1}. \end{aligned} \quad (4.13)$$

(ii) for a Morse interaction potential of the form

$$U(z) = D \{ \exp [-2\alpha(z - z_0)] - 2 \exp [-\alpha(z - z_0)] \} :$$

$$\begin{aligned} \left\langle \phi_{nE} \left| \frac{\partial}{\partial z} \right| \phi_{n'E'} \right\rangle_z &= \frac{\bar{m}}{\alpha} \left[\sinh \left(\frac{2\pi}{\alpha} k_{nE} \right) \sinh \left(\frac{2\pi}{\alpha} k_{n'E'} \right) \right]^{1/2} \\ &\times \left[\cosh \left(\frac{2\pi}{\alpha} k_{nE} \right) - \cosh \left(\frac{2\pi}{\alpha} k_{n'E'} \right) \right]^{-1} \frac{\bar{A}_{k_{nE}} + \bar{A}_{k_{n'E'}}}{[\bar{A}_{k_{nE}} \cdot \bar{A}_{k_{n'E'}}]^{1/2}} \end{aligned} \quad (4.14)$$

with the definitions

$$\bar{A}_{k_{nE}} = |\Gamma(\frac{1}{2} - i k_{nE}/\alpha - \bar{K})|^2; \quad \bar{K} = (2\bar{m}D)^{1/2}/\alpha. \quad (4.15)$$

These expressions are valid if $k_{nE} \neq k_{n'E'}$ and it can be demonstrated that for $k_{nE} = k_{n'E'}$ the couplings are strictly zero. Taking account of this circumstance, it is easy to show from (4.13) and (4.14), that for $k_{nE} \simeq k_{n'E'}$:

$$\left\langle \phi_{nE} \left| \frac{\partial}{\partial z} \right| \phi_{n'E'} \right\rangle_z \simeq \frac{\bar{m}}{\pi} \mathcal{P} \left(\frac{1}{k_{nE} - k_{n'E'}} \right) \quad (4.16)$$

for the two potentials considered here. In Appendix A we show that this type of coupling which produces persistent effects only depends on the asymptotic wavefunctions.

In order to solve the perturbation problem in the $\mathbf{K}$ matrix formalism with the renormalization procedure discussed in § 2, we only need the couplings between states with the same asymptotic energy (see discussion of the shift given by (2.11) and also reference [10]). This gives for the cases of interest:

(i) Exponential interaction:

$$\begin{aligned} V_{n, n+1} &= \left[\frac{n + \frac{1}{2} \pm \frac{1}{2}}{2} \right]^{1/2} \frac{2\bar{m}}{\alpha} \left[\sinh \left(\frac{2\pi}{\alpha} k_n \right) \sinh \left(\frac{2\pi}{\alpha} k_{n+1} \right) \right]^{1/2} \\ &\times \left[\cosh \left(\frac{2\pi}{\alpha} k_n \right) - \cosh \left(\frac{2\pi}{\alpha} k_{n+1} \right) \right]^{-1}. \end{aligned} \quad (4.17)$$

(ii) Morse interaction potential:

$$\begin{aligned} V_{n, n+1} &= \left[\frac{n + \frac{1}{2} \pm \frac{1}{2}}{2} \right]^{1/2} \frac{\bar{m}}{\alpha} \left[\sinh \left(\frac{2\pi}{\alpha} k_n \right) \sinh \left(\frac{2\pi}{\alpha} k_{n+1} \right) \right]^{1/2} \\ &\times \left[\cosh \left(\frac{2\pi}{\alpha} k_n \right) - \cosh \left(\frac{2\pi}{\alpha} k_{n+1} \right) \right]^{-1} \frac{\bar{A}_{k_n} + \bar{A}_{k_{n+1}}}{[\bar{A}_{k_n} \cdot \bar{A}_{k_{n+1}}]^{1/2}} \end{aligned} \quad (4.18)$$

with the definitions

$$\bar{A}_{k_n} = |\Gamma(\frac{1}{2} - i k_n/\alpha - \bar{K})|^2; \quad k_n = [2m(E - n - \frac{1}{2})]^{1/2}. \quad (4.19)$$

5. TRANSITION PROBABILITIES

We now proceed to derive an explicit form for the transition operator (2.23) for the case of inter-continuum coupling between adjacent continua, so that

continuum-continuum coupling terms are given by equation (4.17) or (4.18). Let us define an on-the-energy-shell F matrix :

$$\mathbf{F} = (1 + i\pi V)^{-1} \quad (5.1)$$

which can be utilized to express the T and the S matrices in the following form :

$$\mathbf{T} = \mathbf{F}V, \quad (5.2)$$

$$\mathbf{S} = 1 - 2\pi i \mathbf{F}V. \quad (5.3)$$

Equation (5.1) can be written in the alternative form :

$$\mathbf{F} = 1 - i\pi V \mathbf{F} = 1 - i\pi \mathbf{F}V. \quad (5.4)$$

Substitution of (5.2) into (5.4) results in

$$\mathbf{T} = (i\pi)^{-1} (1 - \mathbf{F}), \quad (5.5)$$

which together with (2.12) yields

$$P_{nn'} = |\delta_{nn'} - 2F_{nn'}|^2. \quad (5.6)$$

We have thus expressed the transition probabilities in terms of the T matrix. Turning now to the specific coupling scheme presented in § 4 we shall express the inter-continuum coupling terms (4.17) and (4.18) in the form

$$V_{nn'} = g_{n'}(E) \delta_{n, n'+1} + g_n(E) \delta_{n, n'-1}, \quad (5.7)$$

where $g_n(E) \equiv V_{n, n+1} \equiv V_{n+1, n}$. The matrix equation (5.4) with the special form of the coupling (5.7) is solved in Appendix B where we show that the $\mathbf{F}$ matrix can be expressed in the explicit form :

$$\begin{aligned} F_{n, n'} &= \frac{Q_\alpha \bar{Q}_\beta}{Q_N} \prod_{j=\alpha}^{\beta-1} (-i\pi g_j); \quad n \neq n' \\ &= \frac{Q_n \bar{Q}_n}{Q_N}; \quad n = n' \end{aligned} \quad (5.8)$$

where $\alpha = \min(n, n')$ and $\beta = \max(n, n')$. Q_α and Q_β are polynomials defined by the recurrence relations

$$\left. \begin{aligned} Q_0 &= Q_1 = 1, \\ Q_{j+1} &= Q_j + \hat{N}_{j-1} Q_{j-1}; \quad j = 1, 2, \dots \end{aligned} \right\} \quad (5.9)$$

and

$$\left. \begin{aligned} \bar{Q}_{N-1} &= \bar{Q}_{N-2} = 1, \\ \bar{Q}_{j-1} &= \bar{Q}_j + \hat{N}_j \bar{Q}_{j+1}, \end{aligned} \right\} \quad (5.10)$$

where $\{\hat{N}_j\}$ is a set of (dimensionless) interference parameters :

$$\hat{N}_j = \pi^2 |g_j|^2. \quad (5.11)$$

Equations (5.6) and (5.8) provide a general, analytical, quantum mechanical expression for the probabilities of vibrational excitation in the collinear collision

of an atom with a harmonic diatomic molecule. The advantages of the present approach which rests on the K matrix formalism are threefold. First, it is gratifying to obtain an analytical solution for a model system which is relevant for the study of vibrational excitation and relaxation and of molecular photo-fragmentation. Up to date [10] analytical expressions were obtained only within the framework of the Born approximation. Secondly, the present quantum mechanical treatment results automatically in a unitary scattering matrix. Third, multiquantum transitions, such as P_{02} are properly incorporated in our theoretical scheme, while first-order transition probabilities completely fail in this case.

Two further observations concerning the general features of our results are in order. We notice that the transition amplitudes for the $n \rightarrow n'$ transition are expressed in terms of products of first-order inter-continuum coupling terms $\prod_j (-i\pi g_j)$ multiplied by a retardation factor $r = Q_\alpha \bar{Q}_\beta / Q_N$. As we have shown in Appendix B $0 < r < 1$. From the point of view of general methodology it is worthwhile to note that the F matrix is related to the Möller wave-operator.

The above analytical treatment for the T matrix is dependent on the harmonic approximation made for the oscillator. If, for instance, the collision is that of an atom with a Morse oscillator [4(b)], all channels are coupled. A first-order K matrix treatment in relative coordinates would also be possible with the use, however, of a numerical algorithm to determine the T matrix.

Finally it must be stressed that the ITFITS semi-classical method [15] can yield excellent results only after a somewhat artificial symmetrization of energies in order to satisfy the principle of detailed balance. The fact however that it is based on relative coordinates indicates that this choice is a very efficient one. That this is also the case for a complete quantum-mechanical treatment will be demonstrated in the next section.

6. NUMERICAL RESULTS

To provide a detailed comparison between the present treatment, previous analytical approaches [10] and exact numerical calculations [4], we have conducted a series of calculations corresponding to (1) K matrix formalism [(5.6) and (5.8)] in relative coordinates without renormalization, with the inter-continuum coupling terms being given by (4.17) or (4.18) with k_n and $k_{n\pm 1}$ being replaced by $\bar{k}_n$ and $\bar{k}_{n\pm 1}$ respectively. (2) K matrix method [(5.6) and (5.8)] in relative coordinates with renormalization, so that the intercontinuum coupling terms are given by (4.17) or (4.18). (3) K matrix formalism [(5.6) and (5.8)] in the linearized version of the distorted wave approximation, the coupling terms being given by (4.12) together with (4.13) or (4.14).

We have made tests for all the parameters for which numerical exact results are available [4, 5]. We present in figures 1 to 8 the most significant of these tests.

6.1. Exponential potential $U(z) = A \exp(-\alpha z)$

The two parameters which are involved in any such calculation are m (cf. equation (2.1)) and α (the constant A does not affect the results). For each of the four reported cases, we have represented P_{01} and P_{02} as a function of energy

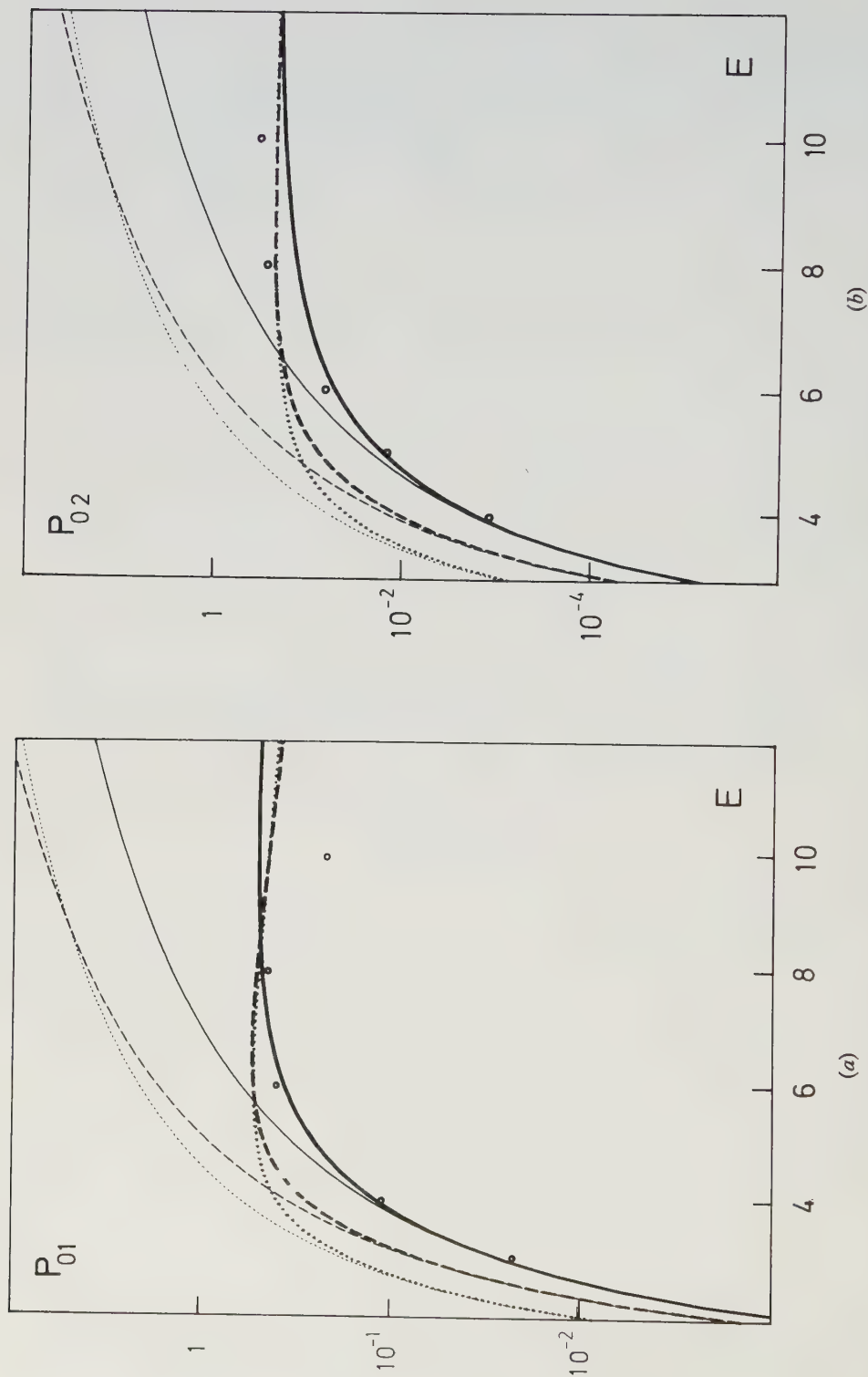
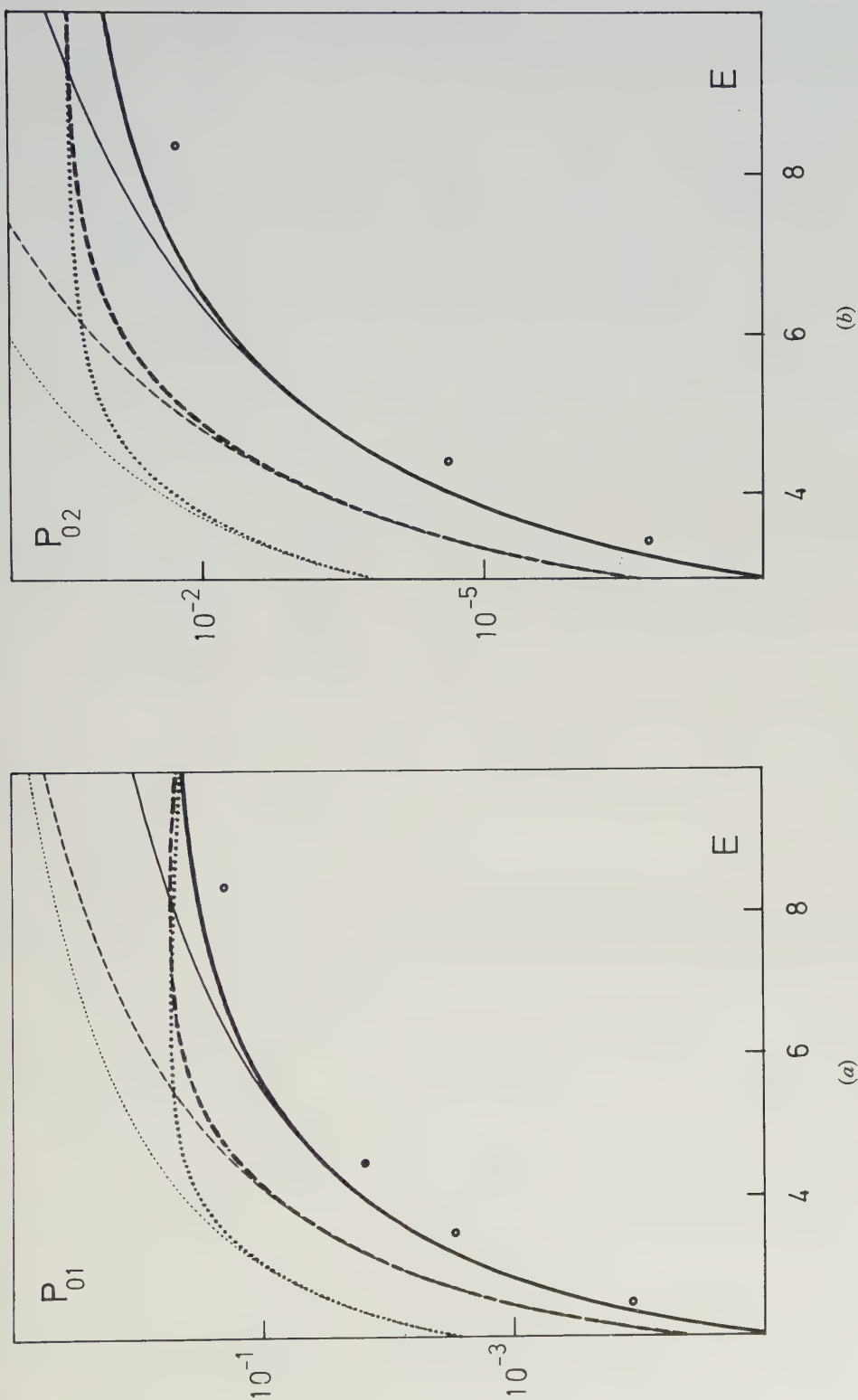
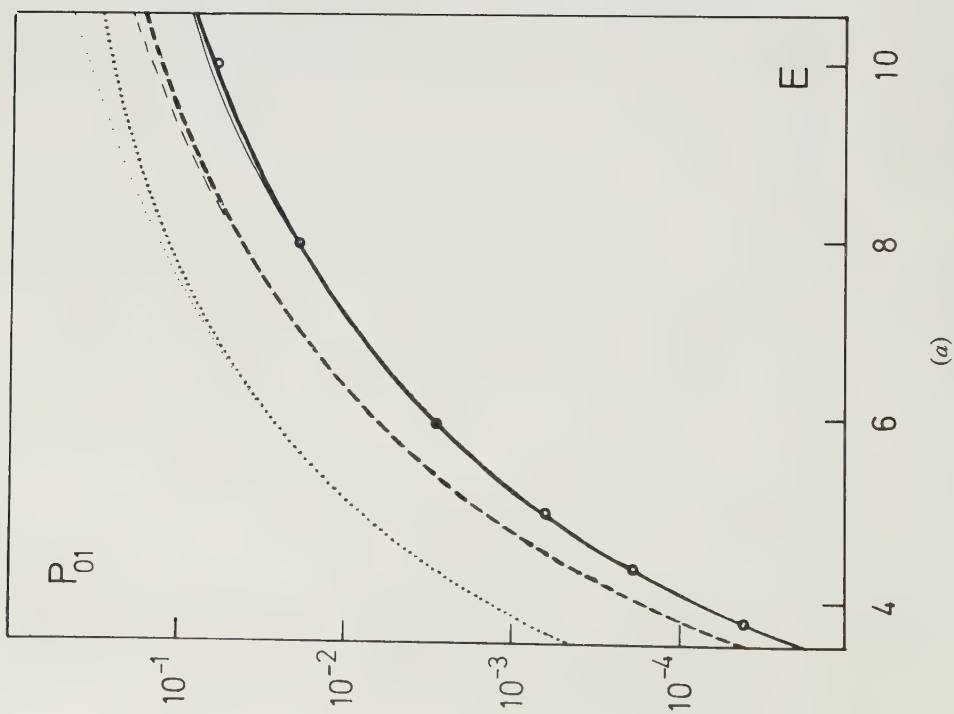
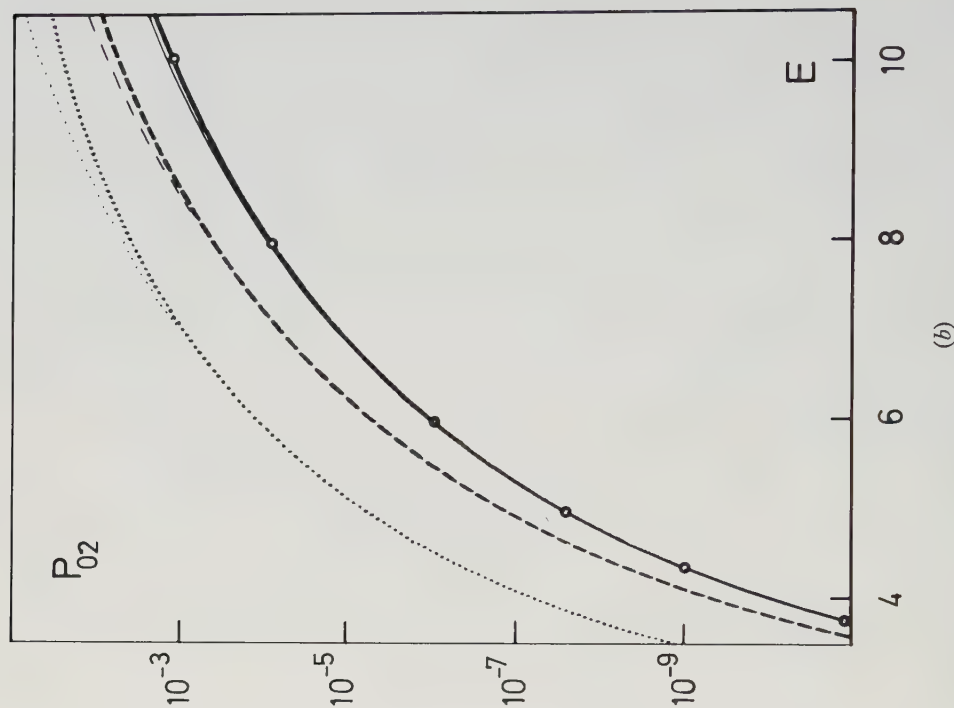


Figure 1. Single and double quantum jump probabilities as functions of energy for $m = \frac{2}{3}$ and an exponential potential with $\alpha = 0.3$. The circles are the exact points of reference [4]. Relative coordinates without (....) or with (—) renormalization, DWA (---). The heavy curves are $\mathbf{K}$ matrix results, the lighter ones the low order approximations discussed in the text.

Figure 2. Same as figure 1 for $m = \frac{5}{4}$ and $\alpha = 0.2973$.



(a)



(b)

Figure 3. Same as figure 1 for $m=0.5$ and $\alpha+0.114$.

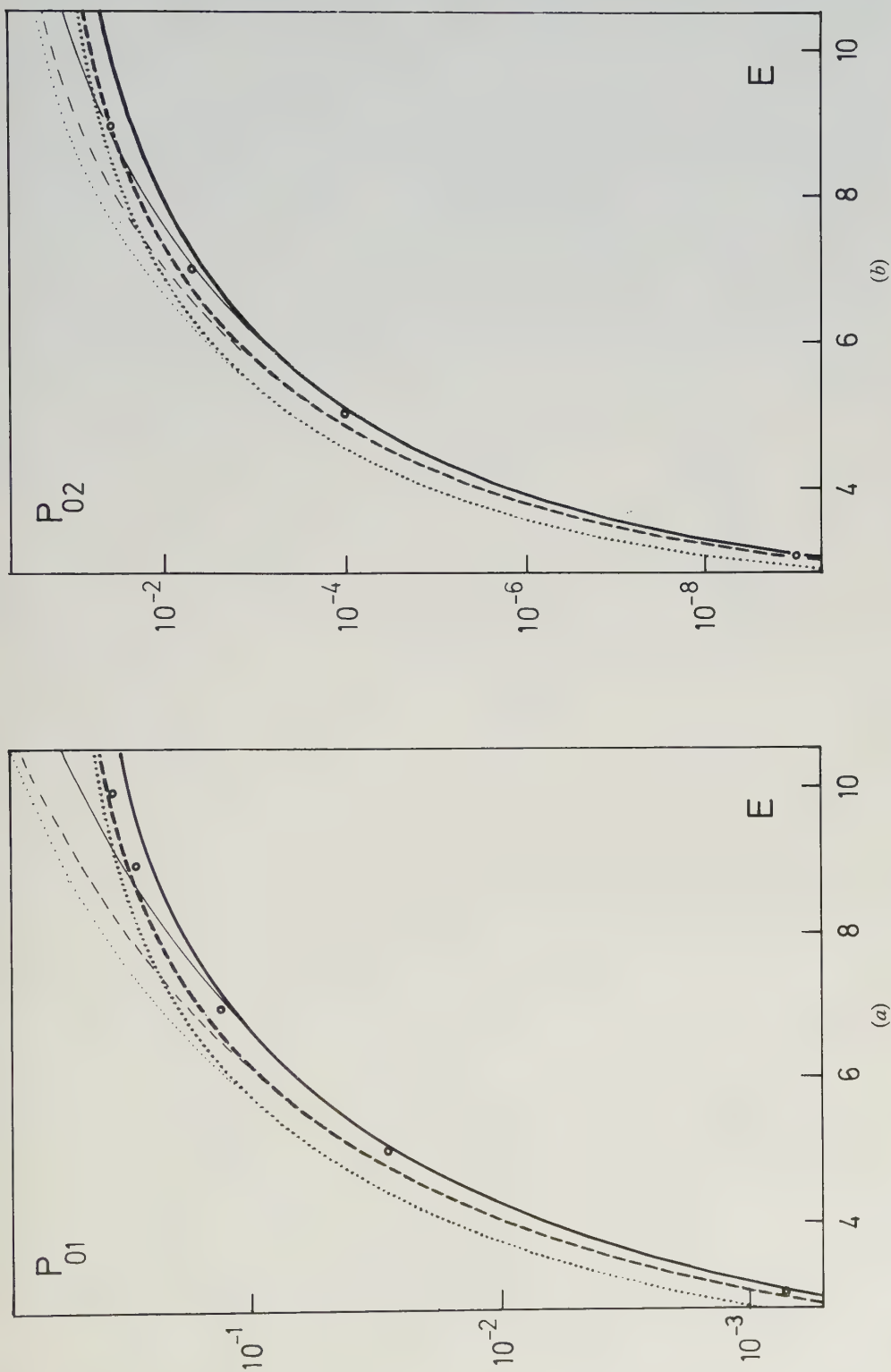


Figure 4. Same as figure 1 for $m=0.2$ and $\alpha=0.114$.

in the various approximations mentioned above. The first-order Born approximation $4\pi^2|V_{01}|^2$ for P_{01} and the second-order expression $4\pi^4|V_{01}|^2|V_{12}|^2$ for P_{02} are also shown, as well as the exact numerical results. We observe, as expected, that the $\mathbf{K}$ matrix treatment affects P_{01} and P_{02} whenever P_{01} to first order is large (say ~ 0.5 or more). This occurs for physically accessible energies when α is large [17]. Figures 1 and 2 ($\alpha=0.3$) show the drastic effect of making use of the reaction operator for all the approximations. This is a very good illustration of the use of this formalism since the first-order probabilities become very large for energies of $5\hbar\omega$ and upwards, even exceeding unity. It is to be noticed that the relative coordinates' approach with renormalization is producing satisfactory results, better than the two other approaches, not only at low energy, as reported previously [10], but also at the energies when the $\mathbf{K}$ matrix formalism starts affecting the results. Figures 3 and 4, on the contrary, show that for a smaller α ($\alpha=0.114$), in the range $E < 10\hbar\omega$, there are only small changes in the probabilities, the larger changes occurring for the smaller m . In these

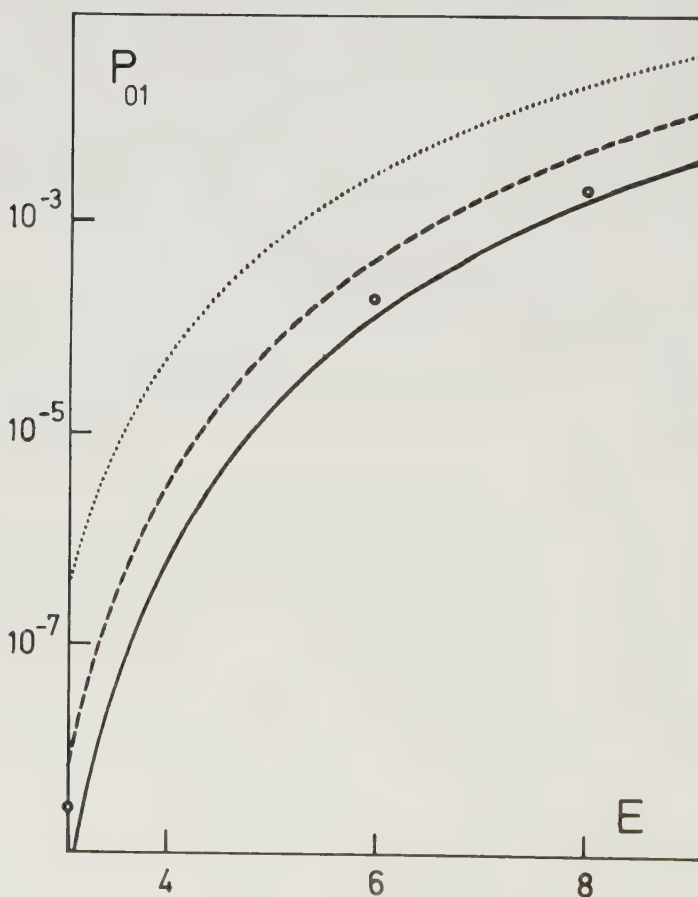


Figure 5. Single quantum jump probabilities as a function of energy for $m=0.5$ and a Morse potential with $D=0.1$ and $\alpha=0.065$. The circles are the exact points of reference [5 (c)]. Same conventions for couplings as in figure 1. $\mathbf{K}$ matrix and first-order results are indistinguishable.

two examples the relative coordinates with renormalization give extremely good results, for probabilities which differ by as much as eight orders of magnitude. In figure 4 we observe that for E approaching 9 or $10 \hbar\omega$, the distorted wave method becomes better.

6.2. Morse potential

In making a similar study for the Morse potential we have been limited by the available exact results [5] which correspond only to P_{01} and bear on parameters and energies leading to either small first-order probabilities, or very similar results for all three methods. Figures 5 and 6 are examples of the first kind. The $\mathbf{K}$ matrix results differ only very slightly from the first-order ones. As noted before [10 (b)] the relative coordinates treatment with renormalization is working extremely well when the depth of the Morse potential is in the range of that corresponding to many systems of interest [5 (b)]. Figures 7 and 8, on the other hand show spectacular $\mathbf{K}$ matrix effects, the exact results being well accounted for by the three methods, with a slight advantage for the distorted wave procedure.

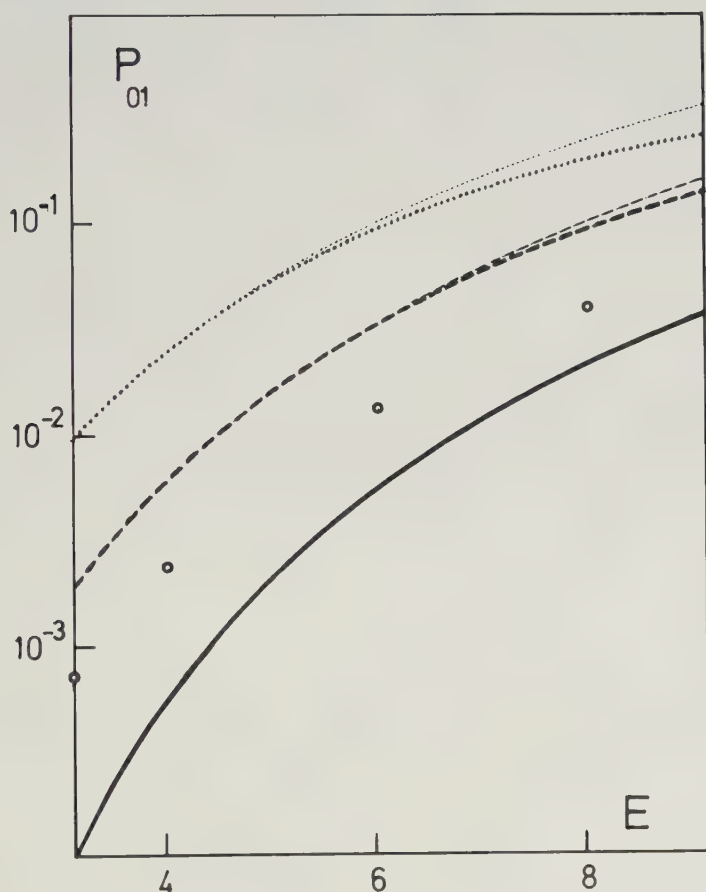


Figure 6. Same as figure 5 with $D=1$.

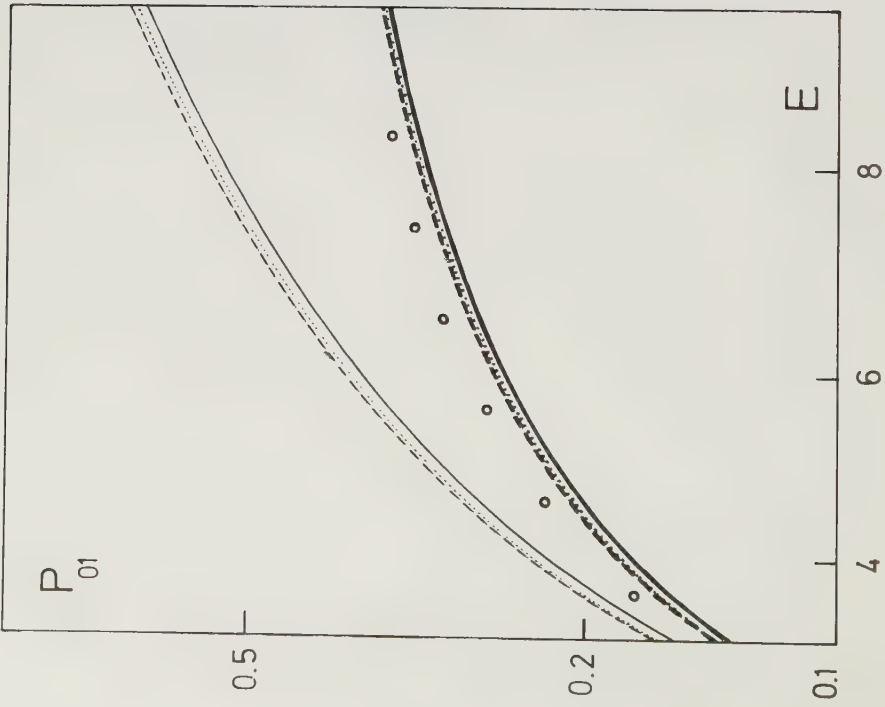


Figure 7. Same as figure 5 with $m=0.0218$, $D=0.5295$ and $\alpha=0.0527$. The exact points are from reference [5 (a)].

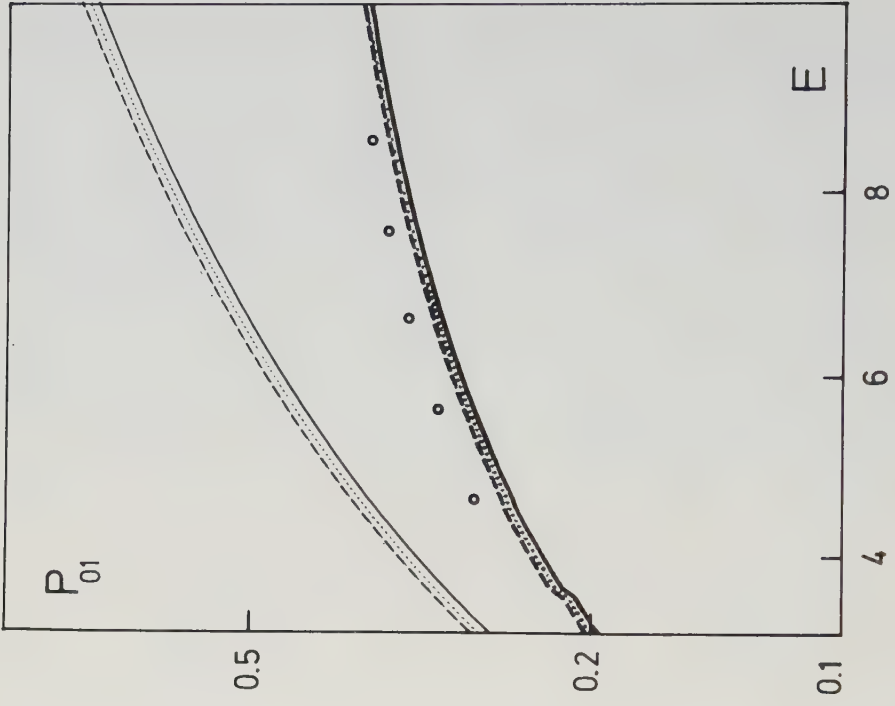


Figure 8. Same as figure 5 with $m=0.0218$, $D=1.059$ and $\alpha=0.0745$. The exact points are from reference [5 (a)].

7. CONCLUSIONS

We have shown that for weak atom-diatom interaction (i.e. small α , low E) a first-order treatment in relative coordinates with renormalization give very good results. On the other hand, for large transition probabilities (i.e. large α , high E), the corrections introduced by the $\mathbf{K}$ matrix are important. In general the $\mathbf{K}$ matrix formalism with renormalization results in a satisfactory physical picture. These calculations are based on simple analytical formulae and can be readily applied to the problem of molecular photofragmentation.

APPENDIX A

The inter-continuum coupling calculated from the asymptotic wave functions

The channel wavefunctions behave asymptotically as

$$|\psi_{nE}^0(y, z)\rangle \underset{z \rightarrow \infty}{\sim} |\chi_n(y)\rangle \frac{2\bar{m}}{\pi \bar{k}_{nE}} \cos(\bar{k}_{nE}z + \bar{\varphi}_{nE}). \quad (\text{A } 1)$$

The inter-continuum coupling calculated from these functions contains the integral

$$l = \int_0^\infty dz \cos(\bar{k}_{nE}z + \bar{\varphi}_{nE}) \frac{d}{dz} \cos(\bar{k}_{n'E'}z + \bar{\varphi}_{n'E'}). \quad (\text{A } 2)$$

Using

$$\lim_{a \rightarrow \infty} \int_0^a \exp(ikz) dz = i\mathcal{P}\left(\frac{1}{k}\right) + \pi\delta(k), \quad (\text{A } 3)$$

we obtain for l :

$$l = -\frac{\bar{k}_{n'E'}}{2} \left[\frac{\cos(\bar{\varphi}_{nE} + \bar{\varphi}_{n'E'})}{\bar{k}_{nE} + \bar{k}_{n'E'}} - \cos(\bar{\varphi}_{nE} - \bar{\varphi}_{n'E'}) \mathcal{P}\left(\frac{1}{\bar{k}_{nE} - \bar{k}_{n'E'}}\right) \right]. \quad (\text{A } 4)$$

Changing the lower limit of integration in (A 2) or replacing the asymptotic functions by the true functions can only affect that part of (A 4) which remains bounded for $\bar{k}_{nE}$ approaching $\bar{k}_{n'E'}$. Thus we conclude that for any potential the inter-continuum coupling contains the principal part distribution $\mathcal{P}(1/(\bar{k}_{nE} - \bar{k}_{n'E'}))$.

APPENDIX B

An explicit form of the F matrix

Substituting (5.7) in (5.4) results in

$$F_{nn'} = a_{n'n} - i\pi g_n F_{n+1, n'} - i\pi g_{n-1} F_{n-1, n'}. \quad (\text{B } 1)$$

Considering a fixed value of n' we get an equation for each value of n . One can thus obtain the following set of N equations:

$$a_n = \delta_{nn'} - i\pi g_n a_{n+1} - i\pi g_{n-1} a_{n-1}, \quad n = 0, 1, \dots, N-1, \quad (\text{B } 2)$$

where we have defined, $F_{nn'} \equiv a_n$. Let us try a solution of the form

$$\left. \begin{aligned} a_n &= \frac{a_{N-1} \tilde{Q}_n \prod_{j=0}^{n-1} (-i\pi g_j)}{\prod_{j=0}^{N-2} (-i\pi g_j)}, \quad n \geq n', \\ &= \frac{a_0 Q_n \prod_{j=n}^{N-2} (-i\pi g_j)}{\prod_{j=0}^{N-2} (-i\pi g_j)}, \quad n \leq n', \end{aligned} \right\} \quad (\text{B } 3)$$

Where $Q_n, \tilde{Q}_n$ are some functions of n to be determined by our set of equations. Substituting (B 3) in (B 2) for $n \neq n', n' \pm 1$ results in the following expressions for $Q_n, \tilde{Q}_n$:

$$\left. \begin{aligned} Q_0 &= Q_1 = 1, \\ Q_{j+1} &= Q_j + \hat{N}_{j-1} Q_{j-1}, \end{aligned} \right\} j = 1, 2, \dots \quad (\text{B } 4)$$

and

$$\left. \begin{aligned} \tilde{Q}_{N-1} &= \tilde{Q}_{N-2} = 1, \\ \tilde{Q}_{j-1} &= \tilde{Q}_j + \hat{N}_j \tilde{Q}_{j+1}, \end{aligned} \right\} j = N-2, N-3, \dots \quad (\text{B } 5)$$

where $\{\hat{N}_j\}$ is a set of (dimensionless) interference parameters:

$$\hat{N}_j \equiv \pi^2 g_j^2. \quad (\text{B } 6)$$

At this stage we are left with three undetermined quantities a_0, a_{N-1} and $a_{n'}$ which will be determined by three equations for $n = n'$ and $n' \pm 1$, which we did not consider. Utilizing (B 3) we can rewrite these three equations in the following form:

(a) The equation for $n = n' + 1$ yields

$$a_{n'} = \frac{a_{N-1} \tilde{Q}_{n'}}{\prod_{j=n}^{N-2} (-i\pi g_j)}. \quad (\text{B } 7)$$

(b) The equation for $n = n' - 1$ gives

$$a_{n'} = \frac{a_0 Q_{n'}}{\prod_{j=0}^{n-1} (-i\pi g_j)}. \quad (\text{B } 8)$$

(c) The equation for $a_{n'}$ results in

$$a_{n'} = 1 - i\pi \left[\frac{g_{n'} a_{N-1} \tilde{Q}_{n'+1}}{\prod_{j=n'+1}^{N-2} (-i\pi g_j)} + \frac{g_{n'-1} a_0 Q_{n'-1}}{\prod_{j=0}^{n'-2} (-i\pi g_j)} \right]. \quad (\text{B } 9)$$

Solving for a_0 we get

$$a_0 = \frac{\bar{Q}_{n'} \prod_{j=0}^{n'-1} (-i\pi g_j)}{\xi(n')}, \quad (\text{B } 10)$$

where

$$\xi(n') = Q_{n'+1} \bar{Q}_{n'} + \hat{N}_{n'} Q_{n'} \bar{Q}_{n'+1}. \quad (\text{B } 11)$$

a_{N-1} is found by equating the right-hand side of equations (B 7) and (B 8). $\xi(n')$, equation (B 11), may be further simplified. Making use of equations (B 4) and (B 5) we have

$$\begin{aligned} \xi(n') &= (Q_{n'} + \hat{N}_{n'-1} Q_{n'-1}) \bar{Q}_{n'} + \hat{N}_{n'} \bar{Q}_{n'+1} \\ &= Q_{n'} (\bar{Q}_{n'} + \hat{N}_{n'} \bar{Q}_{n'+1}) + \bar{Q}_{n'} Q_{n'-1} \hat{N}_{n'-1} \\ &= Q_{n'} \bar{Q}_{n'-1} + \hat{N}_{n'-1} Q_{n'-1} \bar{Q}_{n'} \equiv \xi(n'-1). \end{aligned} \quad (\text{B } 12)$$

Thus $\xi(n')$ is independent of n' and we may write

$$\xi(n') = \xi(0) = \xi(N-1) = \bar{Q}_{-1} = Q_N. \quad (\text{B } 13)$$

We have thus solved equation (B 1) for F . The final result is

$$F_{nn'} = \begin{cases} \frac{Q_\alpha \bar{Q}_\beta}{Q_N} \prod_{j=\alpha}^{\beta-1} (-i\pi g_j), & n \neq n', \\ \frac{Q_n \bar{Q}_n}{Q_N}, & n = n', \end{cases} \quad (\text{B } 14)$$

where

$$\left. \begin{aligned} \alpha &= \min(n, n') \\ \beta &= \max(n, n'). \end{aligned} \right\} \quad (\text{B } 15)$$

Using the recurrence formulae (B 4) and (B 5) we note that :

$$Q_\alpha \bar{Q}_\beta < Q_{\alpha+1} \bar{Q}_\beta < Q_{\beta+1} \bar{Q}_\beta + \hat{N}_{\beta} \bar{Q}_\beta = Q_N \quad (\text{B } 16)$$

which demonstrates that the polynomial fraction in (B 14) is actually a retardation factor :

$$0 < \frac{Q_\alpha \bar{Q}_\beta}{Q_N} < 1 \quad (\text{B } 17)$$

and only when $g_j = 0$ (i.e. trivial case of uncoupled continua) it is equal to unity.

Finally we note that

$$F_{n'n} + (-1)^{n-n'} F_{nn'}^* ; \quad (\text{B } 18)$$

thus F is separable into a sum of hermitian and anti-hermitian matrices :

$$F = F^H + F^{\Delta H}, \quad (\text{B } 19)$$

$$F_{nn'}^H = \begin{cases} F_{nn'} & n + n' = 2q, \\ 0 & n + n' = 2q + 1, \end{cases} \quad (\text{B } 20 \text{ } a)$$

$$F_{nn'}^{AH} = \begin{cases} F_{nn'} & n + n' = 2q + 1, \\ 0 & n + n' = 2q, \end{cases} \quad (\text{B } 20 \text{ } b)$$

where q is an integer.

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